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The Electrolytic Precipitation of Nickel from Phosphate Solutions

THESIS

Presented to the Faculty of the University of Pennsylvania in partial
fulfillment of the requirements for the degree of
Doctor of Philosophy

By

WALTER T. TAGGART, S. B.,
PHILADELPHIA, PA.

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Introduction.

The difficulties attending the gravimetric determination of nickel are such as to suggest the need of improved methods. Nickel can be completely and quantitatively precipitated by the electric current from solutions of nickel sulphate to which ammonium sulphate and ammonia have been added, from solutions of the double cyanides, the double oxalates, and sulphate mixed with alkaline acetates, tartrates and citrates or from ammoniacal solutions.

Fresenius and Bergmann* have said that nickel cannot be precipitated from solutions of its salts containing free mineral acids, but that it can be precipitated from such solutions after the addition of the alkali salts of acetic, tartaric and citric acids.

Smith and Fernberger† have shown that nickel can be completely precipitated from solutions of the sulphate by precipitating the nickel with disodium hydrogen phosphate, dissolving the nickel phosphate in a slight excess of phosphoric acid and electrolyzing the solution. They describe the deposit as dull-gray in color, resembling the appearance to some extent of the platinum dish. The deposit contained phosphorus. Further they say, "notwithstanding the precipitation of the metal was complete, the attempts to separate it in this way from manganese and chromium were fruitless."

It has been the purpose of this investigation to determine the best conditions for the electrolytic precipitation of nickel, free from phosphorus, from phosphate solutions and if possible to effect the separation of nickel from other metals. The general plan is similar to that given above with such changes as may prove necessary.

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* Zeit. für anal. Chem. 19, 315.

† Jour. Am. Ch. Soc., vol. XXI, p. 1005.

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Experimental.

All chemicals used were carefully examined as to purity; the nickel sulphate was the best obtainable from Messrs. Eimer and Amend and was free from cobalt, the disodium hydrogen phosphate was recrystallized several times to insure the removal of any iron that may have been present, and the phosphoric acid was also proved to be free from iron. The nickel sulphate solution contained approximately one-tenth of a gram of metal in ten cubic centimeters, the disodium hydrogen phosphate was of specific gravity 1.038, and the phosphoric acid had a specific gravity of 1.347. The electrolysis was conducted in ordinary platinum dishes, using a flat platinum spiral as anode, the dish being made the cathode. Cover glasses were used to prevent evaporation.

Ten cubic centimeters of nickel sulphate solution containing .1070 gram of metal were incompletely precipitated with varying amounts of disodium hydrogen phosphate, the nickel phosphate dissolved in phosphoric acid and the solution electrolyzed under the following conditions:

	No. 1.	No. 2.	No. 3.
N. $D._{100}$, ampere ..	.8	.9	.95
Volts	7.0	7.5	6.5
Dilution, cc.	125	125	125
Temperature	50°	50°	65°
Time, hours	5	5	5
Disodium hydrogen phosphate, cc. ...	6.3	7.5	6.5
Phosphoric acid, cc.	1.4	1.5	1.5
Nickel found, gram	.1029	.0946	.1049

The deposits of nickel were dull-gray and metallic in appearance. They contained phosphorus. The precipitation was incomplete, due to the presence of free sulphuric acid, and for this reason it was decided to first completely precipitate the nickel as phosphate and then dissolve it in a slight excess of phosphoric acid.

Ten cubic centimeters of nickel sulphate containing .1070 gram of nickel were completely precipitated with forty-five cubic centimeters of disodium hydrogen phosphate, the precipitate dissolved in two cubic centimeters of phosphoric acid and the solution electrolyzed with—

	No. 4.
$N. D._{100}$, ampere	.8-1.0
Volts	6.0-7.0
Dilution, cc.	150
Temperature	65°
Time, hours	5
Nickel found, gram	.1070

The precipitation was complete and the deposit bright but it contained phosphorus. During the electrolysis the solution showed a tendency to separate phosphate of nickel around the upper edge of the deposit.

An attempt was next made to prevent the precipitation of the nickel phosphate by increasing the quantity of phosphoric acid, using a lower current and a higher temperature.

Ten cubic centimeters of nickel sulphate solution containing .1070 gram of nickel were completely precipitated with forty-five cubic centimeters of disodium hydrogen phosphate, the nickel phosphate dissolved in three cubic centimeters of phosphoric acid and the solution electrolyzed with these conditions:

	No. 5.
$N. D._{100}$, ampere	.7
Volts	3.5-5.
Dilution, cc.	125
Temperature	74°
Time, hours	3 2-3

The precipitated nickel weighed .1038 gram, was very bright and metallic, and contained only a trace of phosphorus, showing that the presence of phosphorus in the nickel deposits is due to the separation of the phosphate as indicated above, and which in this experiment was prevented by the excess of phosphoric acid.

Being convinced that the incomplete precipitation of nickel was due to too great an excess of phosphoric acid, a solution containing .1070 gram of nickel was completely precipitated with forty-five cubic centimeters of disodium hydrogen phosphate and the precipitate dissolved in two cubic centimeters of phosphoric acid and the solution electrolyzed with:

	No. 6.
N. D_{100}, ampere	.71-.78
Volts	7.0
Dilution, cc.	150
Temperature	50°
Time, hours	4

The nickel deposit weighed .1084 gram and resembled the platinum dish in appearance. It contained phosphorus.

Four solutions, each containing twenty cubic centimeters of nickel sulphate (=.2040 gram nickel), and ninety cubic centimeters of disodium hydrogen phosphate, were electrolyzed with these conditions:

	No. 7.	No. 8.	No. 9.	No. 10.
N. D_{100}, ampere	.72-.80	.72-.80	.9-1.	.9-1.
Volts	6.5	6.5	6.5	6.5
Dilution, cc.	175	175	175	175
Temperature	50°	50°	50°	50°
Time, hours	4	4	5	5
Nickel found, gram	.2138	.2147	.2139	.2148

Here again the precipitation was complete but the deposit contained phosphorus. The influence of a lower voltage was next studied.

To thirty cubic centimeters of nickel sulphate solution (= .3210 gram nickel), one hundred and thirty-five cubic centimeters of disodium hydrogen phosphate were added, and after adding the quantities of phosphoric acid indicated below, the solution was electrolyzed with:

	No. 11.	No. 12.
N. D.$_{100}$, ampere	1.0	1.0
Volts	5.0	5.0
Dilution, cc.	175	225
Temperature	50°	50°
Time, hours	7½	7½
Nickel found, gram	.3222	.3215

The precipitations were complete and the deposits excellent but contained phosphorus.

Another trial was made with two solutions, each containing twenty cubic centimeters of nickel sulphate solution (= .2140 gram of nickel), ninety cubic centimeters of disodium hydrogen phosphate and four cubic centimeters of phosphoric acid. Six volts were used in this case and—

	No. 13.	No. 14.
N. D.$_{100}$, ampere	1.	1.
Volts	6.0	6.0
Dilution, cc.	175	150
Temperature	50°	50°
Time, hours	7	7
Nickel found, gram	.2134	.2133

The precipitation was not complete. The deposit was good but it still contained a little phosphorus. It was concluded from these results that an insufficient quantity of phosphoric acid had been used; therefore, two solutions, each containing twenty cubic centimeters of nickel sulphate solution (= .2040 gram), ninety cubic centimeters of disodium hydrogen phosphate and four and a half cubic centimeters of phosphoric acid were electrolyzed with five volts, as it has already been shown that nickel can be completely precipitated from a phosphate solution with this pressure. The conditions follow:

	No. 15.	No 16.
N. D_{100}, ampere	1.	0.8
Volts	5.0	5.0
Dilution, cc.	150	175
Temperature	50°	50°
Time, hours	6	7
Nickel found, gram	.2123	.2121

The incomplete precipitation here is most likely due to the low voltage. The deposit of nickel contained but a trace of phosphorus.

A solution containing twenty cubic centimeters of nickel sulphate (= .2166 gram nickel), ninety cubic centimeters of disodium hydrogen phosphate and four and a half cubic centimeters of phosphoric acid was electrolyzed with—

	No. 17.
N. D_{100}, ampere	1.1-1.8
Volts	6.0
Dilution, cc.	175
Temperature	50°
Time, hours	7

The nickel deposit weighed .2171 gram. It was bright, adherent and contained a mere trace of phosphoric acid. The supernatant liquid failed to show the presence of nickel with ammonium sulphide or potassium sulphocarbonate.

It was then decided to run a series of tests, using varying quantities of nickel sulphate solution. Disodium hydrogen phosphate and phosphoric acid were used in the same proportion as in the preceding experiment. The conditions existing during the electrolysis were:

Nos.	18.	19.	20.	21.	22.	23.	24.	25.	26.	27.	28.
N. D_{100}	2,0	2,0	4,0	4,0	2,0	3,0	4,0	2,0	3,0	3,0	4,0
Volts	6.	6.	6.	6.	6.	6.	6.	6.	6.	6.	6.
Dilution, c.c.	225	125	200	250	125	175	250	125	175	175	250
Temperature	50°	65°	65°	55°	65°	65°	55°	65°	70°	62°	55°
Time, hours	7	7½	8¼	9½	6¾	8½	9½	7¼	9	9½	9¾
Na_2HPO_4, c.c.	90	90	130	180	90	135	180	90	135	135	180
H_3PO_4, c.c.	4.5	4.5	9.	9.	4.5	6.75	9.	4.5	6.75	6.75	9.
Nickel taken, gram.	.2166	.2166	.4332	.4332	.2166	.3249	.4332	.2166	.3249	.3249	.4332
Nickel found, gram.	.2163	.2161	.4298	.4321	.2165	.3253	.4327	.2163	.3247	.3251	.4321

In every case except No. 18 and No. 28 the precipitation was complete. The nickel was beautifully bright, smooth, adherent and practically free from phosphorus. The success of the process depends greatly on keeping the dish covered and washing down the sides of the dish with water at frequent intervals, to supply water lost by evaporation and to prevent the phosphates from separating out on the dish.

Further experiments were conducted with a solution of nickel sulphate containing .1088 gram nickel in ten cubic centimeters. The conditions of electrolysis were similar to those given above:

	Nos. 29.	30.	31.	32.	33.	34.	35.	36.	37.	38.
N. $D._{100}$	1.–1.75	1.4–1.8	1.–1.5	1 4–1.8	1.25	1.4–1.8	1.25–1.6	1.25–1.6	1.25–1.6	1.25–1.6
Volts	6.	6.	6.	6.	6.	6.	6.	6.	6.	6.
Dilution, c.c.......	125	125	175	175	175	225	230	230	230	230
Na_2HPO_4, c.c......	90	90	90	135	90	135	180	180	180	180
H_3PO_4, c.c.........	4.5	4.5	4.5	6.75	4.5	6.75	9.	9.	9.	9.
Nickel taken, gram	.2176	.2176	.2176	.3264	.2176	.3264	.4352	.4352	.4352	.4352
Nickel found, gram.	.2179	.2181	.2176	.3271	.2180	.3271	.4353	.4355	.4353	.4354
Temperature......	56°	50°	50°	50°	50°	50°	50°	50°	50°	50°
Time, hours	7	7	7	9¼	7¼	9	10	10	10	10

These results need no further explanation. The deposits were equal in appearance if not superior to any deposits of nickel ever obtained in this laboratory. The deposits containing .4352 gram of nickel when dissolved in nitric acid and tested with ammonium molybdate showed but a trace of phosphorus, and this in no way influences the results, for solutions electrolyzed by Fresenius and Bergmann's method* gave exactly the same amount of nickel.

The effect of elevated temperature was next observed. The following were the conditions:

Nos.	39.	40.	41.	42.	43.	44.
$N. D_{100}$	2.4–2.8	2.25	1.80–2.75	1.80–2.75	1.80–2.75	1.80–2.75
Volts	6.	6.	6.	6.	6	6.
Dilution, c.c.	125	175	225	125	125	175
Temperature	88°	88°	88°	82°	80°	80°
Time, hours	2½	5	6¼	3½	4	5½
Na_2HPO_4, c.c.	90	135	180	90	90	135
H_3PO_4, c.c.	4.5	6.75	9.	6.75	5.6	9.1
Nickel taken, gram	.2176	.3264	.4352	.2176	.2176	.3264
Nickel found, gram	.2167	.3265	.4331	.2150	.2161	.3255

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* Zeit. für anal. Chem. 19, 320.

It will be noticed from the above table that in experiment No. 40 only was the precipitation complete and, further, that the time required in a hot solution is five hours instead of seven to ten hours when electrolyzed at the ordinary temperature.

The separation of nickel from manganese, iron, aluminium and chromium was next considered.

To twenty cubic centimeters of a solution of nickel sulphate containing .2180 gram of nickel and twenty cubic centimeters of a manganous sulphate solution containing about .2000 gram of manganese, ninety cubic centimeters of disodium hydrogen phosphate and seven and a half cubic centimeters of phosphoric acid were added and the solution electrolyzed with a current of 5. volts and .9 ampere. The deposit contained manganese and the nickel was not completely precipitated. Two additional attempts were made to separate these metals and resulted unsuccessfully. When a solution containing nickel sulphate and ferrous sulphate was electrolyzed, it was noticed that the iron was almost completely precipitated with the nickel. The separation of nickel from aluminium gave a similar result. It is also impossible to separate nickel from chromium in a phosphoric acid solution, the chromic salt being oxidized to chromic acid, which prevents the complete precipitation of the nickel.

CONCLUSION.

It has been shown that nickel free from phosphorus can be completely precipitated from an acid solution of nickel sulphate containing disodium hydrogen phosphate and free phosphoric acid, a mineral acid; that the deposit is equal to that precipitated by any other known method; that the time factor can be reduced by raising the temperature; that nickel can not be separated from manganese, iron, aluminium or chromium in phosphoric acid solutions, and that chromic salts in the presence of disodium hydrogen phosphate and free phosphoric acid can be oxidized to chromates by the electric current.

The author takes this opportunity of expressing to Dr. Edgar F. Smith his most sincere thanks and appreciation for the suggestions and assistance given him during the course of his work.

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